

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
22 January 2004 (22.01.2004)

PCT

(10) International Publication Number  
WO 2004/007775 A2

(51) International Patent Classification<sup>7</sup>: C21B 13/00,  
C21C 5/56, C22B 5/10, 7/00, 9/10

(21) International Application Number:  
PCT/GB2003/003065

(22) International Filing Date: 15 July 2003 (15.07.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0216484.6 15 July 2002 (15.07.2002) GB

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant and  
(72) Inventor: WARNER, Noel, Alfred [GB/GB]; 40 High  
House Drive, Rednal, Birmingham B45 8ET (GB).

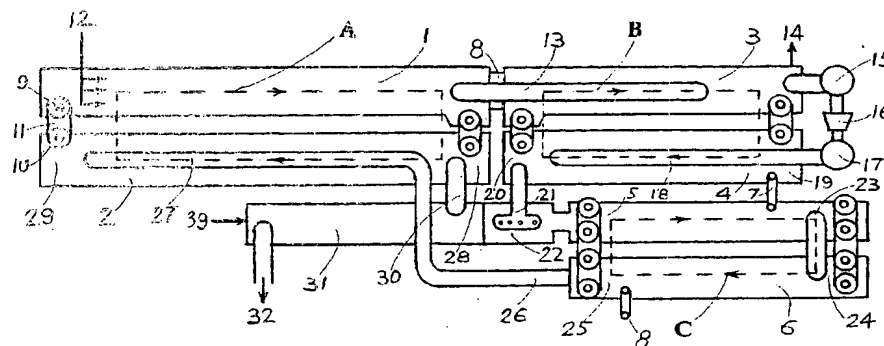
(74) Agents: WARD, David, I et al.; Marks & Clerk, Alpha  
Tower, Suffolk Street, Queensway, Birmingham B1 1TT  
(GB).

**Published:**

— without international search report and to be republished  
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DIRECT PRODUCTION OF REFINED METALS AND ALLOYS



(57) Abstract: The present invention provides a method of reducing metal oxide material to metal comprising the steps of forcibly circulating molten carrier material in a closed loop path serially through a charge reduction zone on one arm of the loop, a combined melt desulphurisation zone and post combustion or heating zone on the other; reducing said metal oxide to solid metal by the carbonaceous material contained within a mixed composite charge of the metal oxide, carbonaceous reductant and flux in said reduction zone, the metal oxide and carbonaceous reductant being utilised in proportions such that the carbon from the carbonaceous reductant is converted to carbon monoxide; reacting carbon monoxide with oxygen in the refining loops downstream from the reduction loop before being combusted to completion in the heating zone at the surface of the molten carrier material so that heat generated by the reaction is transferred to the molten carrier material which is circulated to the reduction zone; separating a metallised raft from said molten carrier material by projecting said metallised raft along into the first refining loop by virtue of the drag force exerted on the metallised raft by the circulating carrier material before the molten carrier material is circulated to the heating zone so that the surface of the molten carrier material which is circulated to the heating zone is substantially free of solid material.

WO 2004/007775 A2

**This Page Blank (uspto)**

## DIRECT PRODUCTION OF REFINED METALS AND ALLOYS

This invention relates to thermal reduction of metal oxide materials, for example iron oxide ores such as haematite, metal oxide ores, e.g. nickel laterite and chromite ores, and deepsea manganese nodules, for the purpose of recovering metallic values therefrom in a refined condition on a continuous basis. The present invention is also concerned with the treatment of steel plant fines, in-plant fines and other secondary materials generated during metallurgical and waste incineration operations.

A method for recovery of metals from oxide materials is disclosed in EP 0266975 and US 4701217, in which smelting reduction of metallic oxide materials, e.g. pelletised iron oxide ore or iron ore fines is effected by contacting such material with a circulating molten carrier material, e.g. molten iron in the case of iron oxide smelting, in a furnace, and by introducing a carbonaceous reductant e.g. coal into the carrier material. The reductant converts the metal oxide to metal, which is assimilated immediately into the molten carrier material in a smelting reduction zone. Carbon monoxide thereby produced is combusted in a heating zone through which the carrier material passes to effect heat recovery. Slag is removed from the carrier material before entering the heating zone. A protective layer of molten material, e.g. lead, which is substantially stationary is maintained below the circulating carrier material to inhibit erosion of the furnace hearth.

Further details of oxide ore smelting by the above melt circulation method are disclosed in "Overview of generic melt circulation technology" by N A Warner in Proceedings of the International Symposium on Challenges in Process Intensification, Montreal, Quebec August 24-29, 1996, The Canadian Institute of Mining, Metallurgy and Petroleum; 269-281, 1996; (ISBN 0-919086-68-3).

EP 0266975 and US 4701217 also make reference to laboratory testwork in which cylindrical compacts of mixed pulverised coal and haematite ore fines were immersed in a liquid metal heat transfer medium (lead) for two minutes. Below 900°C very little reaction occurred, whereas at 1300°C metallisations as measured by bromine-methanol dissolution were in the range 85-90%. It was suggested that if the composite pellets were immersed in hot metal (molten iron containing dissolved carbon) even faster rates could be expected. These

observations were not actually made use of in the processes discussed in these former patents but now they are germane to the present invention.

It has now been discovered that the use of a circulating molten carrier can be advantageous not only in an improved method for reduction of oxide of certain metal oxides but also to recover on a continuous basis refined metal or alloy therefrom in preparation for continuous casting or other downstream finishing operations, e.g. ingot casting, fragmentation, globulation, granulation or if a powdered product is required, atomisation.

According to the present invention, there is provided a method of reducing metal oxide material to metal comprising the steps of forcibly circulating molten carrier material in a closed loop path serially through a charge reduction zone on one arm of the loop, a combined melt desulphurisation zone and post combustion or heating zone on the other; reducing said metal oxide to solid metal by the carbonaceous material contained within a mixed composite charge of the metal oxide, carbonaceous reductant and flux in said reduction zone, the metal oxide and carbonaceous reductant being utilised in proportions such that the carbon from the carbonaceous reductant is converted to carbon monoxide; reacting the carbon monoxide with oxygen in the refining loops downstream from the reduction loop before being combusted to completion in the heating zone at the surface of the molten carrier material so that heat generated by the reaction is transferred to the molten carrier material which is circulated to the reduction zone; separating a metallised raft from said molten carrier material by projecting said metallised raft along into the first refining loop by virtue of the drag force exerted on the metallised raft by the circulating carrier material before the molten carrier material is circulated to the heating zone so that the surface of the molten carrier material which is circulated to the heating zone is substantially free of solid material.

In contra-distinction to the method described in EP 0266975 and US 4701217 the molten carrier material is not involved chemically to a major extent in the reduction process but is there to transport the charge and reaction product materials in the solid state at elevated temperature through an extended path in contact with the molten carrier material which provides the endothermic heat requirements for chemical reactions to take place within a

layer of composite charge material, deposited across the width of the molten carrier material near to one end of the charge arm. A chemical reaction front moves through the layer commencing with solid material submerged in the molten carrier material on the underneath side of the deposited layer, possibly involving an initial formation of solidified crust of the molten carrier material when the charge materials are first deposited at the feed end and then as heat is conducted into the layer, the reaction front progressively moves upward through the layer as it floats away along the arm on the molten carrier material, all the time releasing coal volatiles and gaseous products of reduction into the gas space above the layer which is enclosed by walls and a roof of thermal insulating material. Except for minor addition of oxygen to control carbon deposition and to facilitate a minor degree of sintering of the composite charge surface, no major combustion takes place in this gas space and the conditions throughout are reducing to the newly formed metallic phase, so there can be no question of reoxidation of metallic product taking place in this arm, even if some areas are fully reduced, whilst others are still evolving reducing gases. Accordingly, it is possible to achieve high levels of metallisation of the charge material without elaborate charge preparation or having to reduce the intensity as metallisation approaches completion. The partial sintering of the charge surface, referred to above, occurs at temperatures around 950°C in advance of the somewhat higher temperatures associated with reduction reaching the top surface.

Conduction within agglomerated materials is the principal heat transfer means even at very high temperatures and in the present case this is enhanced by metal not originally in the charge materials infiltrating into the charge layer as production progresses to enhance that produced by reduction. Also sintering phenomena which result ultimately in the formation of a metallised raft emerging from the far end of the arm cause a progressive increase in thermal conductivity the longer the material stays floating down the metallisation arm of the reduction loop. Direct contact with liquid metal eliminates the need for radiative heat transfer in the metallisation arm so there is no special requirement to provide geometric arrangements that ensure access to direct thermal radiation as this is no longer an issue as it is with current technology.

The capillary rise effect occurs as a consequence of hot metal wetting the newly-formed solid metal as a result of gas phase reactions and being drawn into the porous structure by

surface tension. From capillary theory, the rise is directly proportional to the surface tension and inversely proportional to the density of the liquid, so this means that for molten iron the propensity for capillary rise is more than twice as great as that for water entering a porous solid material, assuming that the degree of wetting as measured by the so-called contact angle is the same in both cases.

In the present invention, the infiltration of hot metal by the capillary rise phenomenon as reduction proceeds, effectively reduces the thermal resistance between the molten carrier material and the progressively upwards moving reduction zone to such an extent that heat transfer influences are very considerably reduced so that the kinetics of the chemical reactions become all important, a situation under the control of the process designer in so far as the chemical kinetics can be regulated by specifying particle size of the reacting solids. This means that the most cost-effective solution can be identified for a particular case.

In the absence of heat being transferred from above, as in current practice, the temperature of the top surface of the charge material as seen by the roof and wall enclosure at no time exceeds about 1300°C, so the use of relatively inexpensive and low thermal mass insulating materials becomes a practical proposition throughout the charge arm of the reduction loop. Furthermore, these materials will be unlikely to be exposed to the carry-over of semi-molten oxide components because the reaction gases are no longer passing through the highest temperature zone in their passage to the gas space above the charge. With established rotary hearth processing, for example, the situation is reversed. By all these means reduction rates achievable by the present invention are potentially faster than those associated with rotary hearth furnaces, operated with more expensive refractories at higher temperature levels.

As a further consequence of no major combustion taking place in the charge arm, the problem of fines being blown off the charge material and adhering to the wall of the furnace in a semi-molten condition causing trouble to facilities, including accretion formation requiring periodic removal, are very considerably reduced. The principal combustion processes all occur elsewhere in the overall circuit where fines generation is no longer a major issue. Also, the charge end of the metallisation arm is relatively cool in

comparison with the temperatures needed from the outset in processes employing rotary hearth furnaces for treating feed agglomerates, so if any solid accretions are formed in the front end of the arm, these will not be partially fused and will be removable with relative ease in any case. As the charge layer travels down the arm it will undergo progressive sintering and by the time it is adjacent to roof temperatures approaching the melting point of metallic oxides associated with the charge, fines generation from the sintered surface are most unlikely to occur. However, an open structure for release of coal volatiles and reaction product gases freely into the top gas space is maintained throughout.

As an additional measure to ensure that fines are not carried over excessively into the gas flowing above the charge layer, the gas freeboard distance above the solids may be arranged so that local gas velocities are consistent with the propensity for solids entrainment. This means that in many cases the gas velocity has to be relatively low in the charging region with progressive increase permissible as the solids sinter or agglomerate partially, a condition achieved, for example, by profiling the cross-section of the furnace gas space. In any event, even without such profiling it is desirable to arrange for the discharge of evolved gases at the far end from the charge position so that the increase in cumulative gas flow is in contact with solids with progressively longer times to sinter or consolidate. All the above factors contribute to amelioration of potential problems with fines generation, one of the more serious shortcomings of current technology.

There is an additional possible scenario, which again flows principally from the infiltration of molten metal into the charge layer as reaction proceeds. Not only is the thermal conductivity increased but also the average density of the contents of the floating raft is gradually increased as more and more metal is infiltrated by capillary action to fill up the voids beneath the principal reduction zone as it progresses upwards. This has the effect of causing the raft to sink further into the molten carrier material and increases the amount of reduction that takes place by true smelting reduction, involving the carbon dissolved in the molten carrier material. In the limit, this behaviour means that the metallised raft contains considerably less metal than was originally present in the feed. In the extreme case, the metallised raft projected out of the reduction loop is comprised of residual solid metal formed by gaseous reduction, which has not yet had the opportunity to be assimilated into the molten carrier material, in association with slag constituents and

excess coke coal all forming an agglomerated solid structure. Under these circumstances, an increased amount of molten carrier material clearly has to be overflowed along with the metallised raft to the steelmaking loop in order to balance any new metal being added to the molten carrier material in the reduction loop itself.

The mixed charge to the charge arm of the reducing loop is comprised principally of carbonaceous material, metal oxide material and usually a suitable flux, e.g. lime, limestone or dolomite with particle size requirements determined by preliminary laboratory testing. In some cases it may be desirable to introduce a degree of compaction into the mixed charge constituents as they are deposited onto the moving surface of the molten carrier material using means well-known to those skilled in the art. Also it may be advantageous in some cases to deposit a filter cake from a horizontal belt filter to be discharged onto the melt surface after initial in-line drying. However, in many cases simple mechanical mixing of the constituents will be all that is required.

The vigorous reaction and ebullition that might have taken place and caused an unacceptable loss of fine material entrained in the evolved gasses during smelting reduction of a very thin layer of deposited solids is precluded to a large extent by depositing the composite charge solids so that an immediate layer in the region of 5 to 10 cm thick effectively physically blankets the surface of the molten carrier material, assisted by the increased thermal mass of the charge in some cases causing an initially frozen crust of molten carrier material on the underneath side of the floating charge layer, slowing down vigorous reduction until the material at the interface reaches temperature of 1100°C or so by which time the charge solids have had an opportunity to consolidate at least to some extent.

The method of the present invention is usually performed with a very large proportion of molten carrier material circulation to metal produced. For example, in the case where the metal oxide is iron oxide, a circulation ratio of 100:1 to 500:1 can be employed in the ironmaking loop, the actual ratio depending upon the nature of the feed and the energy requirements thereof. In a particular example, a circulation ratio of 315:1 is employed, namely for every unit of iron produced, 315 units of molten iron as carrier are circulated



between the reduction zone and the heating zone in the closed loop path. The rate of circulation depends upon the size of the equipment and the required reduction rate.

The metal oxide material incorporated within the composite mixed charge, which forms the layer floating on the molten carrier material, is subjected to reduction to produce the metal, and carbon monoxide is evolved above the surface of the molten carrier material and is preferably passed to the other treatment stages which may optionally include liquid metal based hot gas clean-up or other means of desulphurisation; boosting in pressure; staged partial combustion with oxygen to facilitate melting of the metallised raft and combustion of excess carbon therein; liquid slag formation; and decarburisation of the molten carrier material in at least one (preferably two) downstream melt circulation loops by top blowing and direct flame impingement mechanisms, before being passed to the heating zone of the reduction loop where combustion to carbon dioxide is finally completed.

The temperature of the molten carrier material depends upon the type of metal oxide being reduced and is chosen to ensure that the carrier material is prevented from solidifying. For iron oxide ore reduction the temperature is typically about 1300°C, which is high enough to promote reduction but not high enough to cause melting of the solids in the floating charge layer.

The proportions of metal oxide to carbonaceous reductant depend again upon the metal oxide being reduced and also upon the nature of the carbonaceous reductant. However, the proportions employed will be such as to give carbon monoxide. Thus, it will be usual to operate the process with stoichiometric excess of carbon relative to the amount of oxide to be reduced.

In order to maximize the efficiency of heating of the molten carrier material in the heating zone it is necessary to prevent accumulation of slag or solids in the heating zone. This can conveniently be effected by removing the molten carrier from under the slag or any residual solids in the charge arm before passing it to the heating zone.

The solid metallised raft produced in the reduction melt circulation loop described above next becomes the feed input for at least one further melt circulation loop in order to conduct continuous melting, slag separation and primary refining; the molten metal is then passed (eg. overflows or is siphoned) into at least one further melt circulation loop to effect additional refining and composition adjustment after which the molten metal continuously discharges either by overflowing or by siphonic removal so that it either becomes the product refined metal or alloy or optionally continues on for further refining eg. in a packed tower for countercurrent contacting with argon or other suitable gas under reduced pressure to reduce impurities to ultra-low levels.

The metallised raft comprised of solid metal, unreacted carbon, gangue oxide constituents possibly already reacted to form solid slag compounds and solid fluxes to further aid liquid slag formation and metal refining, is propelled out of the charge arm of the reduction loop into the metallised raft melting and slag formation/separation arm of the first in-line refining loops, utilising the resultant drag force exerted on the raft by the molten carrier material in the charge arm of the reduction loop and possibly assisted by maintaining a shallow depth of molten carrier material on the cross-over interconnecting the two said melt circulation loops to ensure unimpeded continuous transference of the metallised raft onto the surface of a second molten carrier material being circulated in a closed loop path serially through a top blown/flame impingement zone in order to melt the metallised raft, burn excess carbon on one arm of the loop and a second arm on which heating and additional refining processes such as desulphurisation and decarburisation are conducted employing top blowing and liquid flux contacting in concert.

Separation of slag and metal occurs by the solid metal in the metallised raft being assimilated into the molten carrier material and the slag forming a continuous molten layer floating on the molten carrier material down to the far end from the feed input where it either overflows with the molten carrier material into a downstream zone where slag can accumulate for intermittent tapping while the molten carrier material is removed from beneath the accumulated slag for continuous circulation to the other arm of the melt circulation loop using a gas-lift mechanism or siphon, whichever is the more appropriate. Alternatively, the overflow weir can be dispensed with and use made of an electromagnetic dam as developed for continuous strip casting and the like to keep the

molten metal back whilst accumulating a pool of molten slag which can be removed either continuously or intermittently by tapping.

Unlike the reduction loop, the molten carrier materials in the refining loops are involved chemically in the process because the metal being produced is dissolved therein and impurities such as carbon, silicon, sulphur and phosphorus interact thermodynamically with each other in ways that can influence the choice and effectiveness of refining processes to which the molten carrier materials are subjected, it being appreciated that because of the large melt circulation ratios established in the refining loops and already referred to for the reduction loop, the molten product overflowing from these loops is virtually the same as the molten carrier and the melt composition throughout a particular loop is effectively constant and temperature differences in the bulk of the molten carrier throughout are relatively minor.

An optional final step in the process for producing molten refined metal or alloy is to cause the molten metal, either overflowing or being siphoned out from the last of the melt circulation refining loops, to irrigate solid packing elements within a packed tower with molten metal flowing by gravity downwards in the form of droplets and rivulets with a rising gas flow such that true countercurrent contact is maintained between the gas and liquid phases with longitudinal or backmixing reduced to an absolute minimum. A preferred way of achieving this true counterflow is to operate the tower under reduced pressure so that the downward velocity of the liquid metal droplets and rivulets is less than the upwards velocity of the gas. For ultra-low carbon (ULC) steel production, the objective of this countercurrent contacting is to effect the reaction between dissolved carbon and dissolved oxygen by maintaining virtually zero concentration of gaseous reaction product, carbon monoxide, at the base of the solid packing where high purity argon is admitted.

For the UCL Tower Refiner any suitable relatively large packing elements may be used with 100-150 mm MgO or MgO/Al<sub>2</sub>O<sub>3</sub> spinel being a preferred choice. In considering the diameter of the ULC Tower it is important to keep below the so-called flooding condition and also the gas phase pressure drop should only be a minor fraction of the total pressure. For the case of ULC steel, an elaborate vacuum system is not required and all that is

needed is a water ring pump to exhaust the purge gas and its associated carbon monoxide at a pressure in the region of 100mbar.

The method of this aspect of the present invention is suitable for direct coal-based continuous steelmaking from fine coal and iron ore fines. Although it has already been pointed out, the molten carrier material in the reduction loop is not formed directly from the charge material, it is convenient to use hot metal (hot molten iron, impure in the as-smelted state) as the molten carrier material and to add or remove hot metal from the first loop as the on-going process demands. For the other loops, which constitute the continuous steelmaking process, however, the iron produced by reduction forms the carrier material, which is removed, preferably continuously, at a rate which substantially balances the rate of iron production.

There have been many unsuccessful attempts in the past to develop continuous steelmaking. Problems with refractories stand out as the principal contributors to unreliability and excessive operating costs in those processes reaching semi-plant size trials. The source of these problems can be traced back to the aggressive behaviour of molten iron oxide towards refractories, exacerbated by reactor high intensity when oxygen is used directly as in modern steelmaking. When oxygen is used directly to refine hot metal, subsurface formation of carbon monoxide bubbles generate mild explosions throwing molten slags and splashes of metal into the surrounding gas accompanied by further intense reaction of ejected droplets and copious generation of iron oxide fumes.

Besides attack on the refractories, the above scenario generates accretions and other problems which are incompatible with continuous processing. A more moderate approach is needed, preferably one which takes into account legitimate concerns about climate change and greenhouse gas emissions as well as social issues relating to health and safety, sustainability and the environment. Considerable benefits to all these would stem from substitution of oxygen steelmaking with carbon dioxide blowing for decarburisation coupled with efficient post combustion to offset the endothermicity of the reaction chemistry. Oxygen should be used for post combustion of carbon monoxide generated during reduction, but first the carbon monoxide should be partially combusted with oxygen in a step-wise fashion to provide the gaseous oxidant for top blowing along with

water vapour derived from hydrogen in the reductant for steelmaking rather than using oxygen directly. Sequential combustion of the carbon monoxide also permits heat to be generated for melting the metallised raft in the first of the steelmaking loops, whilst maintaining iron as the thermodynamically stable phase so iron oxide is not formed at unit activity and the problem of refractory attack is greatly reduced. In addition, except for uncontaminated nitrogen from air separation, processes of the future must move ideally towards zero gas emission after sequestration of the carbon dioxide. Clearly, oxygen processing is needed but not in the way it is used in current steelmaking practice.

As we move towards a hydrogen economy, there will still be a need to decarburise iron melts containing minor amounts of carbon to produce refined steel. In this case the gas phase will be principally hydrogen diluted with nitrogen or just hydrogen. The gaseous mixture required for primary and secondary steel making will be  $N_2/H_2O$  again ensuring that no free oxygen comes into direct contact with carbon containing molten iron anywhere in the process.

It is now well established that interfacial chemical kinetics play an important role in the reaction of carbon dioxide or water vapour with carbon dissolved in molten iron during the decarburisation process of primary steelmaking. The slow chemical step involving dissociative adsorption is not observed with oxygen, where gaseous diffusion and liquid phase mass transfer can both influence the rate of decarburisation. Accordingly, to moderate the steelmaking reaction, carbon dioxide and water vapour are the preferred oxidants. This is especially the case when the molten iron being decarburised contains dissolved sulphur, as it undoubtedly will in any real steelmaking situation. This is because sulphur slows down the dissociative adsorption reaction on the gas-liquid interface.

The lesser intensity referred to above is turned into a positive advantage in the present invention, where it is imperative that sub-surface nucleation and growth of carbon monoxide bubbles must not be allowed to occur in the interests of avoiding explosive ejection of metal droplets into the gas space followed by further intense reaction with sparking and copious fume generation, all of which are incompatible with continuous processing as discussed earlier. This is a key requirement, which must be taken into

account in specifying the methods to be used in the melt circulation steelmaking loops for continuous steelmaking without disruptive ebullition and ejection of melt from bubbles as they burst through the flowing melt surface with consequential skull or accretion build-up on the walls and roof of the reactor, which would eventually necessitate shutdown of the continuous steelmaking plant. In the present invention, this is secured by adapting the processing conditions so that the supply of carbon to the melt surface by liquid phase mass transfer throughout all of the steelmaking loops is always adequate to prevent oxygen atoms from diffusing into the molten metal to such an extent that concentrations of both oxygen and carbon in the bulk molten iron reach supersaturation levels sufficient to induce the decarburisation reaction to occur spontaneously beneath the surface.

For the particular case of coal-based continuous steelmaking, two steelmaking loops are preferred. The first is top blown to effect primary decarburisation, whilst in the second loop what has been termed "open-channel" decarburisation is promoted under increased melt circulation rate. For both loops, steady-state conditions are established such that gas phase mass transfer, interfacial chemical kinetics and liquid phase mass transfer all balance each other.

Particular examples of the invention as applied to direct coal-based continuous steelmaking will now be described with reference to the accompanying drawings in which:-

Fig. 1 is a schematic general arrangement in plan view of the plant for direct coal-based continuous steelmaking, when steel scrap, hot briquetted iron (HBI), or direct reduced iron (DRI) are readily available and their use is economical.

Fig. 2 is a schematic general arrangement in plan view for direct coal-based continuous steelmaking for a stand-alone plant based on virgin ore as the only source of iron units.

Referring now to Fig. 1, the plant comprises six furnace hearths 1, 2, 3, 4, 5 and 6, which are arranged in pairs to form three inter-linked melt circulation loops A (a charge reduction loop), B and C (first and second refining loops) formed by interconnecting the first and second hearths 1 and 2 (constituting a charge reduction and a

desulphurisation/heating zone respectively), the third and fourth hearths 3 and 4 (constituting a melting zone and a desulphurisation/decarburisation zone) and the fifth and sixth hearths 5 and 6 respectively. Under steady operating conditions, molten metal is caused to overflow or be otherwise taken out of the second and third loops B and C by conductively heated siphons 7 and 8 so that molten metal issuing from these is equivalent to the metal in the composite charge initially added to the top surface of the molten carrier material at the upstream end of the first hearth 1, together with any scrap or pre-reduced material added to the circuit and shown in Fig. 1 as 12. At the downstream end of the first hearth 1, a channel or ramp 8 is provided to permit solid material (metallised raft) floating on the surface of the molten carrier material in the first hearth 1 to be propelled or projected into the third hearth 3 onto the surface of the molten carrier material in the first refining loop B, along with a lesser amount of molten carrier material from the reduction loop A, corresponding to new metal assimilated into the carrier material in reduction loop A, resulting from any smelting reduction taking place between the floating charge layer, ultimately becoming an agglomerated solid structure referred to as the metallised raft as it progresses downstream in the first hearth 1.

Forced melt circulation in all loops is effected by R-H type snorkels 9 connected to vertical bodies 10 linked to each other by horizontal members 11 to form vacuum-tight refractory-lined vessels, which can function either as gas-lift pumps or siphons depending on whether or not an inert gas is injected into the upleg snorkels. Under reduced pressure melt is drawn up into both snorkels 9 and the lower regions of the vertical bodies 10 and the horizontal members 11 in each unit to form a channel through which the melt traverses as it flows from one hearth to another along the horizontal member 11. These vessels can be either lowered so that the snorkels 9 are immersed in the molten carrier materials or raised for stand-by or replacement with preheated units on a scheduled maintenance basis.

The very much smaller siphons 7 and 8 have similar features to the units described above, but because the melt flow rates in these siphons correspond to the actual metal production rate, steps may need to be taken to independently heat the flowing metal by direct resistance heating or so-called conductive heating.

The composite charge 12, comprised of well-mixed iron ore fines, fine coal and preferably burnt lime flux, is distributed uniformly onto the surface of the molten carrier material towards the upstream end of the first hearth 1 to form a floating charge layer 5 to 10 cm in thickness, whilst being heated from beneath by the molten carrier material. Coal volatiles and reaction product gases are discharged from the gas space above the floating solid charge into a refractory-lined gas header duct 13, which forms the manifold for an array of top blowing lances with concentric controlled oxygen admission so that the metallised raft floating in the third hearth 3 is melted to form a liquid slag layer, whilst the metallics are assimilated into the molten carrier material. Slag is removed at the downstream end of the third hearth 14 either continuously or intermittently from a pool of molten slag formed when the molten metal is held back by an electromagnetic device or dam similar to that being developed for continuous casting applications.

The gases flow from the third hearth 3 into a hot gas clean-up (HCGU) facility, which incorporates a combined liquid-metal quench and desulphurisation tower 15, a turbo-booster 16 and a liquid-metal based gas reheater 17. In other embodiments (not shown), the gases are arranged to flow into the HCGU facility from the first hearth.

With its pressure now increased, the hot gas from the HCGU flows into a refractory-lined header duct 18, which forms the manifold for an array of top blowing lances with further controlled concentric oxygen addition so that carbon dioxide and water vapour become the oxidant gases rather than oxygen itself for primary or major decarburisation of the molten carrier metal in the fourth hearth 4 using direct flame impingement to provide both the thermal requirements and the gaseous reactant for the endothermic decarburisation reaction.

Besides providing the principal decarburisation requirements, the fourth hearth 4 is used to effect flux-based desulphurisation, whilst the dissolved oxygen content of the iron is relatively low and the carbon level sufficiently high to sustain this requirement. Accordingly, desulphurisation flux is added at the upstream end of the fourth hearth 19 and removed at its downstream end 20.



The hot gases from the fourth hearth 4 discharge into a refractory-lined header duct, which forms the manifold for an array of top blowing lances 21 with further concentric controlled oxygen addition to effect melting of preheated steel scrap or prereduced material in a pool of molten metal 22, which overflows liquid scrap into the fifth hearth 5 where the melt is flowing at an accelerated rate in the end in which open-channel decarburisation of the melt siphoned from the fourth hearth 4 is effected by contacting the melt in the fifth hearth 5 with the oxidising gases leaving the pool melter 22 under turbulent flow conditions. Because of the lesser amount of decarburisation that occurs in the second refining loop C, the sensible heat of the gases leaving the pool melter 22 is more than adequate to provide the endothermic requirements of secondary decarburisation before the gas flows into the sixth hearth 6 via the refractory-lined cross-over gas duct 23. Because the carbon level throughout the second refining loop C is low, the melt is effectively steel for general purpose applications and the dissolved oxygen level is high enough to conduct flux-based dephosphorisation by adding powdered flux at the upstream end 24 of the sixth hearth and removing flux at the downstream end 25.

After passing along the length of the sixth hearth 6, the hot gases discharge into a refractory-lined transfer duct 26, which becomes the manifold 27 for an array of top blowing lances with major concentric oxygen addition (or other suitable configuration such as mutually opposed jets) to effect combustion to completion of the gases emitted initially from the reduction loop A via the off-take 13 into the first of the refining (steelmaking) loops B. This major combustion utilises direct flame impingement onto the molten carrier material in the second hearth 2 to contribute towards the post combustion energy needed to sustain ironmaking in the first hearth 1.

A small amount of a desulphurisation flux, which wets the melt surface and spreads across it to form a continuous thin film on the surface of the molten carrier material, is added at the upstream end 28 of the second hearth 2 and taken away at its downstream end 29. This contributes to desulphurisation in the circuit, but most importantly raises the emissivity of the molten carrier material and so considerably enhances heat transfer by radiation. The very hot combustion gases are discharged into a refractory-lined off-take 30, possibly with stave cooling within the refractory lining, directly into a countercurrent radiant scrap preheater 31, in which a sloping hearth plus a mechanical device is used to

contact selected steel scrap 39 to effect major scrap preheating and possible partial melting, before the scrap or other reduced material passes into the pool melter 22. The off-gas from the scrap preheater leaves the plant at 32 and can be used in a heat recovery steam generator (HRSG) for advanced power generation.

Vacuum degassing of steel using the RH process is established practice throughout the world. By injecting argon into a single upleg, molten steel circulation at rates up to about 200 tonne per minute can be obtained and this is now regarded as state of the art in the steel industry. However, elaborate vacuum plant as used in RH degassing is not needed for the melt circulation systems in the present invention. Argon can be used as the lift gas but it may be preferable to use the desulphurised gas arising from ironmaking whilst it is still not oxidising iron, because argon is needed elsewhere in the circuit, particularly if ultra-low carbon steel (ULC) is to be produced continuously using the molten steel discharging from 8 as the feed into the Tower Refiner described previously.

It must be stressed that the overall energy implications of melt circulations as shown schematically in Fig. 1 are minimal. To circulate melt through a closed loop path is a function of the product of the rate at which melt is circulated times the total liquid head to be pumped against. For the present case, differences in level throughout the whole system are mainly due to frictional effects and other phenomena associated with open channel fluid flow at high throughput. Accordingly, the pumping heads can be kept small by design so that very large circulation rates can be employed for the various molten carrier materials without consuming undue amounts of energy.

For the steel industry world-wide, the ultimate vision is perpetual recyclability with steel scrap being recycled again and again with input from iron ore only utilized to accommodate growth in demand. This embodies the desirable concept of environmental sustainability, requiring conservation of natural resources (iron ore and coal), minimizing the production of CO<sub>2</sub> in the first instance and sequestration of whatever CO<sub>2</sub> is produced to combat climate change and global warming.

To maximize scrap melting or charging of DRI, HBI etc. if so desired, all of the gases emitted from the ironmaking loop A need to be utilized together in both of the steelmaking loops B

and C. Ideally, the smelting reduction gases in total need to be passed directly to the metallised raft melting arm (hearth 3) of the primary steelmaking loop A and partially combusted with oxygen with direct flame impingement using an array of top blow lances to effect iron melting and liquid slag formation as the metallised raft floats along with the circulating iron carbon melt with phase disengagement completed when a molten slag layer free from associated iron is established towards the downstream end of the arm in question, in advance of slag removal from the circuit.

To ensure high iron recovery, metallic iron is maintained as the thermodynamically stable phase by controlling the oxygen addition in both the smelting reduction arm (hearth 1) of the ironmaking loop A and the metallised raft melting arm (hearth 3) of the primary steelmaking loop B.

The principal supply of heat for smelting reduction is by melt circulation in the ironmaking loop A. Soot formation as coal is devolatilised and reduction commenced is precluded by minor oxygen admission above the charge material as it floats down the charge arm (hearth 1) of the ironmaking loop A but the mixed gases are never allowed to become oxidizing to metallic iron, either here or after the flame impingement top blow arrangement for melting the metallised raft in the first steelmaking loop B. This is a unique feature, only feasible in a melt circulation system, and guarantees very high iron recovery without oxidation losses. It assumes, of course, that the retention time in the ironmaking arm (hearth 1) is adequate to achieve a high degree of metallisation in the first instance. Once solid metallic iron is formed it will be impossible to lose any of this by solution in the slag, nor can it be oxidized within the ironmaking furnace itself.

Direct flame impingement was selected so that metallic iron at unit activity can be melted directly without relying on dissolution in the Fe-C melt. Similarly, the processes involved in slag formation are accelerated by this approach.

Very little of the heat required in the steelmaking loops is derived from the sensible heat of the circulating melt. This has important implications relating to the design of the above bath enclosures. Low thermal mass insulating materials, commercially available, are incorporated throughout the walls and roofs of both steelmaking loops A and B and for the charge side

(hearth 1) of the ironmaking loop A. It is only the desulphurisation/heating arm (hearth 2) of the ironmaking loop A which may require a high specification refractory enclosure, although even here it may be feasible to use low thermal mass and relatively inexpensive insulating materials currently being developed. Obviously this must have a major impact in terms of capital cost savings. It also facilitates easy access to the hearths, if needed, and generally reduces the structural requirements because the materials involved are lightweight in comparison with brickwork or castable refractories.

The hot gases undergo hot gas cleanup (HGCU) involving a liquid metal quench, which incorporates sulphur removal to a very high level as well as removal of particulate solids, before being boosted in pressure to around 0.5 to 1 bar gauge and reheating again by liquid metal direct heat exchange. The gases are returned to the steelmaking loop B at about 1350°C for partial combustion with oxygen to provide the chemical and thermal requirements for major decarburisation of Fe-C melt by direct flame impingement under non-splashing top blow conditions on the desulphurisation flux arm (hearth 3) of the primary steelmaking loop B. The momentum of the jets clears the flux away and mixes it to assist desulphurisation, whilst promoting liquid phase mass transfer of dissolved carbon from the bulk of the liquid metal to the interface, where the endothermic reactions with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  take place.

The top blow lances are designed so that the supply of gaseous oxidant to the liquid metal interface at steady state is balanced by the supply of carbon by liquid phase mass transfer. Allowance is also made for the kinetics of the dissociative adsorption of both  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , including the inhibiting effects of sulphur. The resulting steady state conditions are such that sub-surface CO bubble formation cannot take place. Laboratory experiments using the electromagnetic levitation technique have established that sparking or copious fume generation will not occur under these relatively mild conditions.

The gases during decarburisation may gain enough CO by reaction that they may leave the primary steelmaking loop A with metallic iron again as the stable thermodynamic phase. Further controlled addition of oxygen is made to these gases in another top-blow flame impingement arrangement, this time directed at a pool of molten iron, which is essentially a cul-de-sac off the second refining loop C for what is termed open-channel decarburisation. This pool receives partially melted steel scrap from a radiant heater in the form of a sloping

hearth, leading directly into the pool and fired by the very hot gases from the second hearth. The overflow from the pool is liquid scrap, which joins the main melt circulation flow, any non-metallic residues being incorporated into the dephosphorisation flux layer as it floats down this arm (hearth 5) of the open-channel decarburisation loop C. The hot gas mixture then transverses the length of the open-channel decarburisation arm (hearth 5), where a clean metal surface permits further decarburisation to a low level without sparking or fume emission and then the hot gases are ducted to the heating arm 2 of the ironmaking loop A where further oxygen is added for full combustion before exiting to the sloping hearth radiant heater for partial melting of steel scrap at a temperature at between 1700-1800°C at the inlet with countercurrent contacting of the incoming scrap feed.

The gases ultimately leave the radiant heater at around 850°C for transmission to the heat recovery steam generator (HRSG), which together with the steam tubes associated with the various frozen shells constitute the steam boiler for advanced power generation.

The embodiment described above when applied to plant for continuously producing steel from iron ore fines, when steel scrap, HBI or DRI are both readily available and economic to use, would typically produce three tonnes of steel product from every one tonne of virgin iron units incorporated into the composite mixed feed.

There will always, of course, be a need for creation of value-added products by primary production away from centres of high population and scrap availability and, ideally, new technology must be able to switch easily from high scrap utilisation to 100 pct virgin raw materials, if the situation so demands. It is this in-built flexibility that is a key feature of the present invention. In place of the scrap melting arrangement shown in Fig. 1, the gases in 21 flow directly to the fifth hearth 5, the pool melter 22 and the radiant scrap preheater are both eliminated.

This means that extra combustion is available in the second hearth and to prevent this from over heating it is necessary not to fully combust the gases therein but to pass the very hot gases now containing residual CO and H<sub>2</sub> directly to a Waste Heat Boiler (WHB), probably with CO<sub>2</sub> recirculation to moderate temperatures. In the event, more electricity than needed for air separation and CO<sub>2</sub> liquefaction will be generated. Depending on the proximity of

other plant nearby or other in-plant usage, some of the power generated would be available for export to the grid if such an opportunity exists in centres away from densely populated areas. Alternatively, if steel scrap is not readily available and the use of HBI or DRI is uneconomic, then this becomes the preferred option with export of electricity to the national grid.

Referring now to Fig. 2, a stand-alone plant retains the principal features of having six furnace hearths, which are arranged in pairs to form three inter-linked melt circulation loops. Except for the changes discussed above in relation to the non-availability of steel scrap at the right price and assuming that using HBI or DRI is also not economic, the other features in Fig. 2 are essentially the same as those shown in Fig. 1 and corresponding reference numerals are used accordingly. For the stand-alone plant, however, since excess thermal energy is available, it may be desirable to incorporate calcination of limestone 33 to burnt lime 34 into the circuit. This is shown schematically in Fig. 2 as an adjunct downstream of the off-take 30 of the very hot gases from the post combustion arm (hearth 2) of the ironmaking loop A. It involves recycling a stream 35 of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at a temperature at around  $125^\circ\text{C}$  from the exit flue of the WHB to temperate the gas leaving hearth 2 through the off-take 30, which is split into two streams, into one of which powdered limestone 33 is injected. Sufficient residence time is provided in the gas flow path within the calciner 36 to produce burnt lime 34, which is recovered by a cyclone separator 37 and the combined gases 38 then proceed to the WHB. This burnt lime is one of the principal components of the mixed composite charge 12 and may also be used in preparation of the desulphurisation flux 19 and the dephosphorisation flux 24.

The method according to the present invention is not solely applicable to iron oxide ores such as haematite, but is also applicable for example, to the production of refined metal or alloy from the following:

- (1) Chrome ores to form ferrochromium alloys.
- (2) Chromite together with nickel sulphide to make master alloys for stainless steelmaking.
- (3) Chromite and nickel oxide for direct stainless steelmaking.
- (4) Nickel laterites to form ferronickel directly.
- (5) Deepsea manganese nodules to form copper-nickel-iron alloy (furnace alloy).

(6) Manganese ore to ferromanganese alloys.

## CLAIMS

1. A method of reducing metal oxide material to metal comprising the steps of:-
  - (i) circulating a first molten carrier material in a closed solid-state reduction loop serially through a charge reduction zone and a combined melt desulphurisation and heating zone;
  - (ii) circulating a second molten carrier material in a closed melt refining loop serially through a melting zone and a desulphurisation/decarburisation zone
  - (iii) introducing a mixed composite charge comprising a metal oxide and a carbonaceous reductant onto the surface of the carrier material in the reduction zone of the solid-state reduction loop,
  - (iv) reducing said metal oxide to solid metal by the carbonaceous reductant in the reduction zone, the metal oxide and carbonaceous reductant being introduced in step (iii) in proportions such that the carbon from the carbonaceous reductant is converted to carbon monoxide, hydrogen gas also being produced;
  - (v) separating a metallised raft containing the solid metal from said molten carrier material by projecting said metallised raft into the refining loop upstream of the heating zone of the solid-state reduction loop so that the surface of the first molten carrier material which is circulated to the heating zone is substantially free of solid material;
  - (vi) mixing the carbon monoxide and hydrogen formed in step (iv) and partially combusting the mixture in the melt refining loop in order to satisfy the thermal requirements for melting the metallised raft and for the chemical reactions taking place in the desulphurisation/decarburisation zone and providing the gaseous oxygen mixture containing no free oxygen in order to effect decarburisation;
  - (vii) optionally carrying out further partial combustion of the carbon monoxide and hydrogen to melt solid scrap or direct reduced material;
  - (viii) after steps (vi) and (vii), mixing the carbon monoxide and hydrogen with oxygen and completely combusting the mixture well above the melt in the heating zone of the solid-state reduction loop so that although direct flame impingement is facilitated, no unreacted oxygen comes into contact with the melt in providing the full thermal requirements for reduction of the oxide charge materials in the solid state by transfer to the first molten carrier material which is recirculated to the solid-state reduction zone;



- (ix) submitting the carbon monoxide and hydrogen to hot gas cleanup for removal of sulphur and solid particulates prior to step (vi), (vii) or (viii);
- (x) melting the metallised raft in the melting zone of the refining loop and refining the molten metal in the desulphurisation/decarburisation zone, and
- (xi) removing the metal so refined from the refining loop.

2. The method as claimed in claim 1, wherein the composite charge additionally comprises a flux.

3. The method as claimed in claim 2, wherein said flux is selected from lime, limestone and dolomite.

4. The method as claimed in any preceding claim, wherein said metal oxide is selected from one or more of iron, chromium, nickel and manganese oxides.

5. The method as claimed in any preceding claim, wherein the composite charge added in step (iii) forms a layer having a thickness of from 5 cm to 20 cm, preferably 5 cm to 10 cm, on the first carrier material.

6. The method as claimed in any preceding claim, wherein the composite charge is at least partially compacted prior to step (iii).

7. The method as claimed in any preceding claim, wherein the ratio of carrier material to metal to be produced is from 100:1 to 500:1, preferably 200:1 to 400:1.

8. The method as claimed in any preceding claim, wherein the charge reduction zone of the solid-state reduction loop is constituted by a first hearth and the desulphurisation/heating zone is constituted by a second hearth, a flowpath being provided between a downstream end of the first hearth and an upstream end of the second hearth and between a downstream end of the second hearth and an upstream end of the first hearth.

9. The method as claimed in any preceding claim, wherein the melting zone of the refining loop is constituted by a third hearth and the desulphurisation/decarburisation zone is constituted by a fourth hearth, a flowpath being provided between a downstream end of the third hearth and an upstream end of the third hearth and between a downstream end of the fourth hearth and an upstream end of the third hearth.
10. The method as claimed in claim 9, wherein said flowpaths are provided by gas lift pumps or siphons.
11. The method as claimed in any preceding claim, wherein the velocity of the carbon monoxide produced in step (iv) increases toward the downstream end of the charge reduction zone.
12. The method as claimed in any preceding claim, wherein hot gas clean up is effected between steps (iv) and (viii).
13. The method as claimed in any preceding claim wherein any slag produced in step (iv) is removed from the carrier material before the latter is passed into the desulphurisation/heating zone.
14. The method as claimed in any preceding claim, wherein step (v) is achieved by maintaining a shallow depth of the first molten carrier material in a crossover between the melt circulation loop and the refining loop, so that the metallised raft floats on the first molten carrier material and is transferred to the refining loop by drag forces exerted by the first molten carrier material.
15. The method as claimed in any preceding claim, wherein the metal removed from the refining loop in step (viii) is passed to an additional refining loop for further refining..
17. A metal refining apparatus comprising:-
- (i) a solid-state reduction loop comprising first and second hearths, a continuous flowpath existing between a downstream end of the first hearth and an upstream end of

the second hearth and a downstream end of the second hearth and an upstream end of the first hearth,

- (ii) a refining loop comprising third and fourth hearths, a continuous flowpath existing between a downstream end of the third hearth and an upstream end of the fourth hearth and a downstream end of the third hearth and an upstream end of the fourth hearth,
- (iii) means for introducing a composite charge into the upstream end of the first hearth,
- (iv) means for transferring, in use a metallised raft floating on a molten carrier material from the downstream end of the first hearth to the upstream end of the third hearth,
- (v) ducting for transporting gases generated in the first hearth to the third hearth for partial combustion,
- (vi) ducting for transporting the partially combusted gases in the third hearth to the fourth hearth for further combustion,
- (vii) ducting for transporting the partially combusted gases in the fourth hearth to the second hearth for complete combustion with oxygen, and
- (viii) a hot gas clean up unit in the gas flowpath between the first and third hearths or between the third and fourth hearths.

**This Page Blank (uspto)**